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The pH of aqueous solutions in the vicinity of a thin self-doped conducting polyaniline electrode was electrochemically modulated using both cyclic voltammetry and step potential techniques. Changes in pH were measured directly by using a microcombination pH probe. The experimental results demonstrate that the polymer behaves as a proton ejector during oxidation and a proton absorber during reduction. This potential-controlled pH change near the polymer coated electrode may be applied to many fields benefitting from electronic control of the proton environment near an electrode surface, for example, control of enzyme activity.

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**Electronic Control of pH at
Sulfonated Polyaniline Electrodes**

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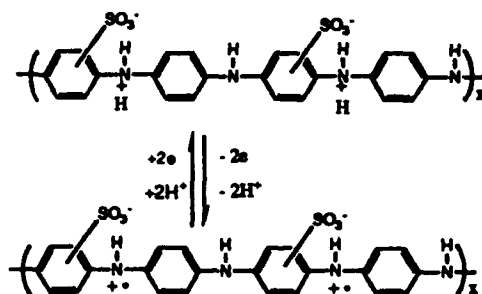
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ABSTRACT

Electrochemical modulation of self-doped sulfonated polyaniline is demonstrated to provide electronic control of pH and enzyme activity in the vicinity of the electrodes.

Typical cyclic voltammograms of the first redox process in different pH solutions of a sulfonated polyaniline film cast on Pt are shown in Fig. 1. In order to obtain a direct evidence that the proton serves as the counterion in this process we used a microcombination pH probe (Microelectrodes, Inc., MI-410) placed on the surface of the film electrode. The response time of the pH probe was less than 5 s. The result of an in situ pH determination during the first redox process is shown in Fig. 2. The response of the pH can be explained in the following redox mechanism of sulfonated polyaniline.



3

covalently bound to the polymer into the surrounding medium. As a result, the pH of the solution in the vicinity of the electrodes is decreased. After the reversal of the scan direction, the flow of cathodic current resulted in neutralization of polarons and absorption of protons, while the pH changes back to its original value. This redox process is an electron-proton transfer mechanism involving an equal number of electrons and protons and exhibits a variation of 59 mV/pH for the half-wave potential.⁶ The direct measurement of the pH change during modulation of the potential supports the mechanism proposed previously.⁶ In order to rule out the possibility of the pH change caused by reduction of oxygen in the aqueous solutions, we examined bare Pt and polyaniline coated Pt electrodes under the same experimental conditions and found no detectable change in pH. These observations clearly show that the pH change which accompanies the redox process tracks the reduction and oxidation of sulfonated polyaniline, and that the release and absorption of protons are reversible.

Figure 3 shows the pH change near the surface of the film electrode caused by a step potential between -0.1 and 0.35 V vs. Ag/AgCl (sat.). A one to one correspondence between applied potential and pH is found. The magnitude of the pH change per volt is dependent on the pH of the electrolyte. For example, the pH change is 3.5 pH/volt in pH \sim 3 solution while the change is 7.5 pH/volt in pH \sim 6 electrolyte.

Sulfonated polyaniline is particularly durable for pH \leq 4 and potential lower than 0.35 V vs. Ag/AgCl (sat.). For example, the optical reflectance of a film on a Pt electrode changed less than 20% after 7 million cycles in 1

M HCl.

The experimental results demonstrate that sulfonated polyaniline behaved as a proton sponge during a redox process. It can change the pH near the surface of the electrode within few tens ms and has high charge efficiency compared to other polymer based pH modulators.⁸ We conclude that it is possible to fabricate an electrically controllable proton sponge or pH modulator as a closed micro-cell. One example of applications of pH modulation is control of the reactivity of pH sensitive enzymes in the vicinity of the sulfonated polyaniline. For instance, we have taken 5 μ l of chymotrypsin (5mg/ml in 0.5 M NaCl) acting on 40 μ l of succinyl-Ala-Ala-pro-phe-4-nitroanilide (5mg/ml in 0.5 M NaCl) placed on the surface of a sulfonated polyaniline coated onto a Pt electrode. The ratio (R) of the absorbances at 375 nm (reacted substrate) to 320 nm (unreacted substrate) varies with the oxidation states of sulfonated polyaniline. For example, for sulfonated polyaniline held at 0.30V, 0.10V and -0.20V vs Ag for a 20 min reaction time, R=1.36, 1.26, and 0.94, respectively, demonstrating electronic control of chemical reactivity of enzymes.

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References

- ¹Huang, W.-S.; Humphrey, B. D.; MacDiarmid, A. G. *J. Chem. Soc., Faraday Trans. I* 1986, 82, 2385-2400.
- ²Orata, D.; Buttry, D. A. *J. Am. Chem. Soc.* 1987, 109, 3574-3581.
- ³Yashima, Y.; Kobayashi, M.; Lee, K. B.; Chung, D.; Heeger, A. J.; Wudl, F. *J. Electrochem. Soc.* 1987, 134, 46-52.
- ⁴Wei, Y.; Focke, W. W.; Wnek, G. E.; Ray, A.; MacDiarmid, A. G. *J. Phys. Chem.* 1989, 93, 495-499.
- ⁵Yue, J.; Epstein, A.J. *J. Am. Chem. Soc.* 1990, 112, 2800-2801.
- ⁶Yue, J.; Wang, Z.H.; Cromack, K.R.; Epstein, A.J.; MacDiarmid, A.G. *J. Am. Chem. Soc.* 1991, 113, 2665-2671.
- ⁷Yashima, Y.; Kobayashi, M.; Lee, K.B.; Chung, D.; Heeger, A.J.; Wudl, F. *J. Electrochem. Soc.* 1987, 134, 46-52.
- ⁸Sawai, T.; Shinohara, H.; Ikariyama, Y.; Aizawa, M. *J. Electroanal. Chem.* 1990, 283, 221-230.

Figure Captions

Figure 1. Typical cyclic voltammograms (50 mV/s) of first redox process of sulfonated polyaniline, where the working electrode was a polymer coated Pt foil, the counter electrode was a Pt foil and the reference electrode was saturated calomel electrode in 1.0 M HCl (—) and pH=3 1 M KCl solutions (- - - -).

Figure 2. pH curve obtained simultaneously with a cyclic voltammogram of sulfonated polyaniline on a Pt electrode in 1.0 M NaCl, pH=3 solution. Scan rate = 10 mV/s.

Figure 3. pH change in the vicinity of sulfonated polyaniline coated Pt electrode upon double step potential between -0.1 and 0.35 V in 1.0 M (pH=5.6) NaCl, the charge was of 0.2 mC.

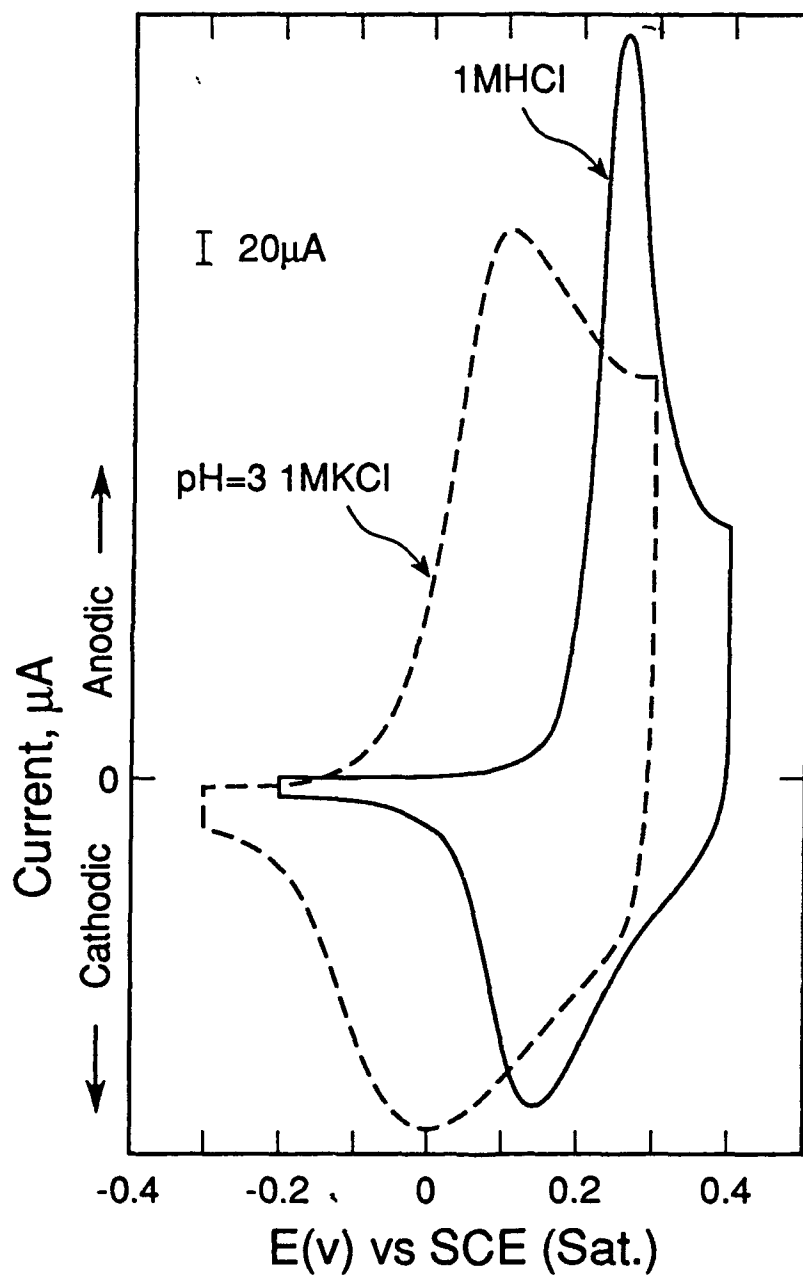
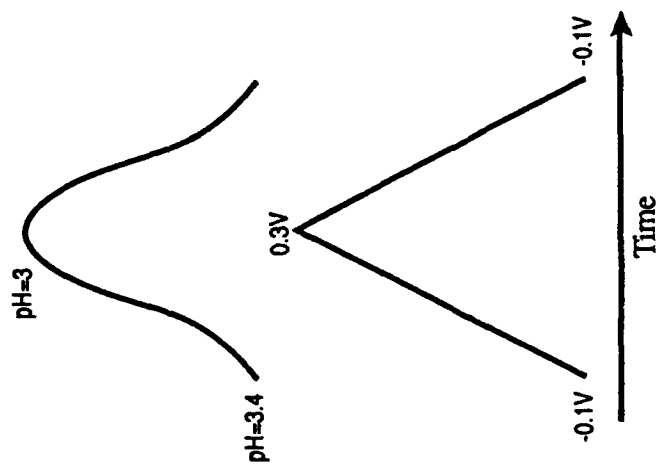


Fig. 1 Yue & Epstein



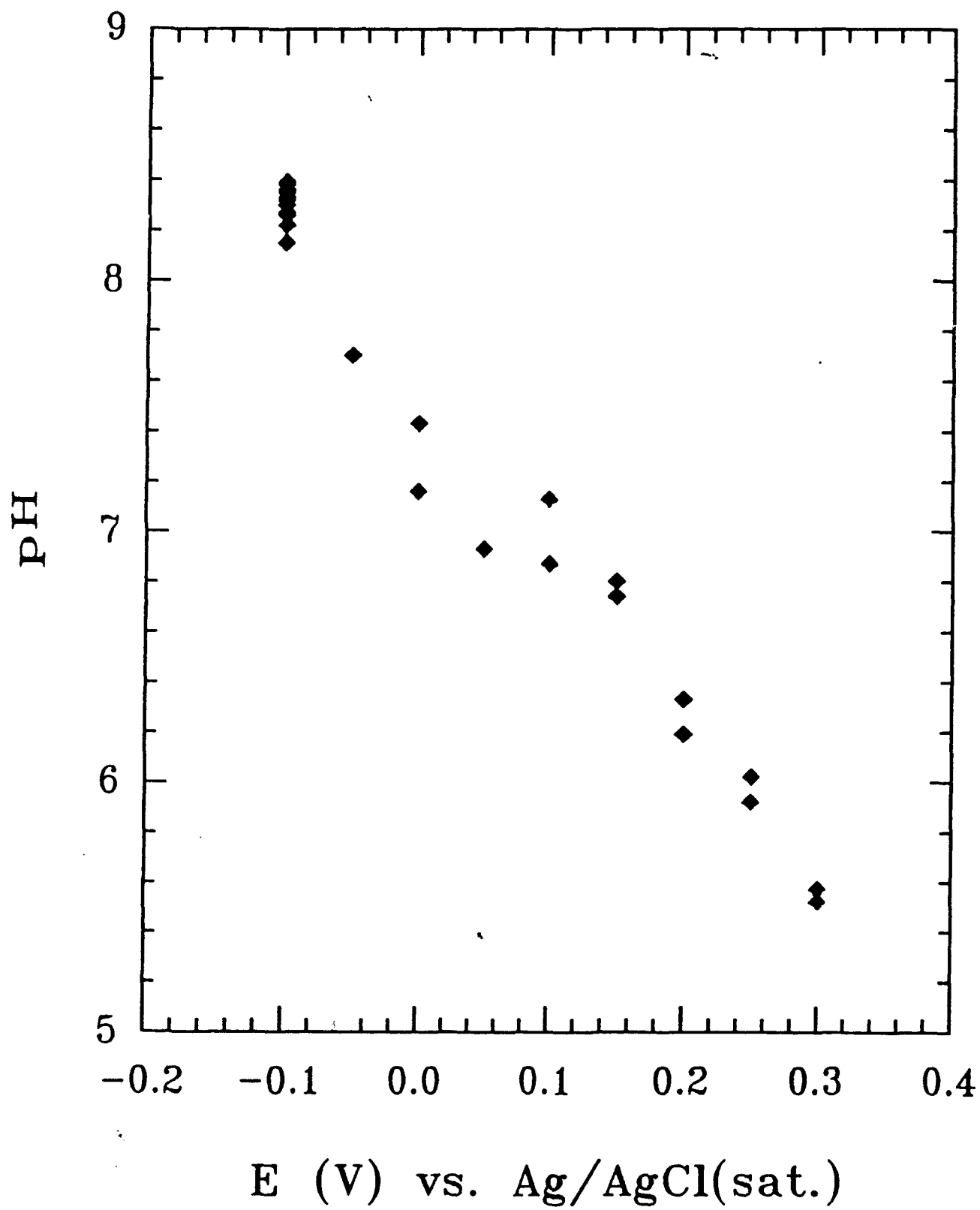


Fig. 3 Yue & Epstein